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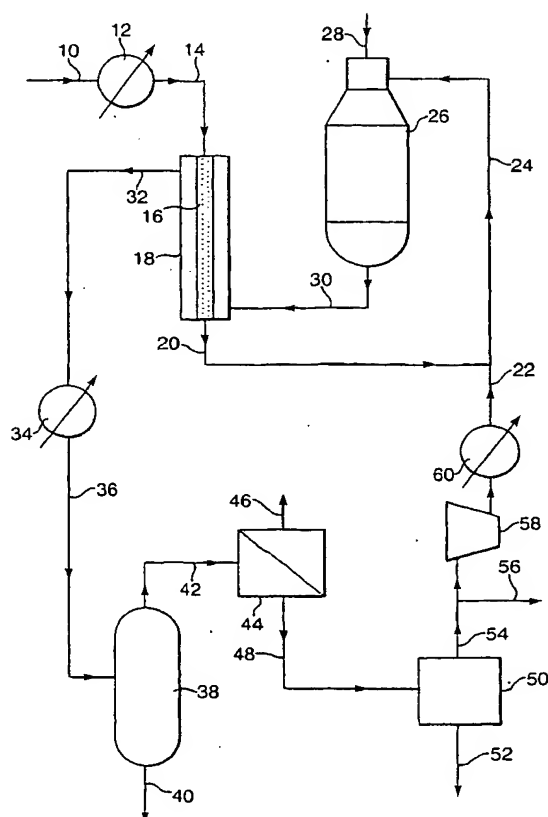
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- (54) Title:** PRODUCTION OF HYDROCARBONS



- (57) Abstract:** Synthesis gas for a Fischer-Tropsch process is obtained by primary steam reforming a hydrocarbon feedstock in tubes in a heat exchange reformer, subjecting the primary reformed gas to secondary reforming and using the hot secondary reformed gas to heat the tubes in the heat exchange reformer. The resultant reformed gas is cooled, de-watered and used to form hydrocarbons in the Fischer-Tropsch process. At least part of the tail gas from the Fischer-Tropsch process is recycled by adding it to the primary reformed gas before secondary reforming.



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European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
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Production of hydrocarbons

This invention relates to the production of hydrocarbons by the Fischer-Tropsch process and in particular to steam reforming and in particular to the production of the synthesis gas for use in that process. The synthesis gas contains hydrogen and carbon oxides and is produced by the catalytic reaction of steam with a hydrocarbon feedstock.

In the Fischer-Tropsch process, a synthesis gas containing carbon monoxide and hydrogen is reacted in the presence of a catalyst, which is typically a cobalt- and/or iron-containing composition. The process may be effected using one or more fixed catalyst beds or using a moving catalyst, for example a slurry of the catalyst in a hydrocarbon liquid. The product hydrocarbon liquid is separated from the residual gas. The reaction may be carried out in a single pass or part of the residual gas may be combined with fresh synthesis gas and recycled to the Fischer-Tropsch reactor. Any residual gas which is not recycled to the Fischer-Tropsch reactor for further reaction is here termed tail gas. Since the reaction of the synthesis gas is incomplete, the tail gas will contain some hydrogen and carbon monoxide. In addition, the tail gas may also contain some light hydrocarbons, e.g. paraffins including methane, ethane, butane, olefins such as propylene, alcohols such as ethanol, and traces of other minor components such as organic acids. It will generally also contain some carbon dioxide, which may be present in the synthesis gas fed to the Fischer-Tropsch reaction and/or is formed by side reactions. Possibly, as a result of incomplete separation of the liquid hydrocarbon product, the tail gas may also contain a small proportion of higher hydrocarbons, i.e. hydrocarbons containing 5 or more carbon atoms. These components of the tail gas represent a valuable source of carbon and hydrogen.

In the present invention at least part of the tail gas is recycled and used as part of the feedstock employed to make the Fischer-Tropsch synthesis gas.

Steam reforming is widely practised and is used to produce hydrogen streams and synthesis gas for a number of processes such as ammonia, methanol as well as the Fischer-Tropsch process.

In a steam reforming process, a desulphurised hydrocarbon feedstock, e.g. natural gas or naphtha, is mixed with steam and passed at elevated temperature and pressure over a suitable catalyst, generally a transition metal, especially nickel, on a suitable support, for example alumina, magnesia, zirconia, or a calcium aluminate cement. In the steam reforming process, any hydrocarbons containing two or more carbon atoms that are present are converted to carbon monoxide and hydrogen, and in addition, the reversible methane/steam reforming and shift reactions occur. The extent to which these reversible reactions proceed depends upon the reaction conditions, e.g. temperature and pressure, the feed composition and the activity of the reforming catalyst. The methane/steam reforming reaction is highly endothermic and so the conversion of methane to carbon oxides is favoured by high temperatures. For this reason, steam reforming is usually effected at outlet temperatures

above about 600°C, typically in the range 650°C to 950°C, by passing the feedstock/steam mixture over a primary steam reforming catalyst disposed in externally heated tubes. The composition of the product gas depends on, inter alia, the proportions of the feedstock components, the pressure and temperature. The product normally contains methane,
5 hydrogen, carbon oxides, steam and any gas, such as nitrogen, that is present in the feed and which is inert under the conditions employed. For applications such as Fischer-Tropsch synthesis, it is desired that the molar ratio of hydrogen to carbon monoxide is about 2 and the amount of carbon dioxide present is small.

In order to obtain a synthesis gas more suited to Fischer-Tropsch synthesis, the primary
10 reformed gas may be subjected to secondary reforming by partially combusting the primary reformed gas using a suitable oxidant, e.g. air or oxygen. This increases the temperature of the reformed gas which is then passed adiabatically through a bed of a secondary reforming catalyst, again usually nickel on a suitable support, to bring the gas composition towards
15 equilibrium. Secondary reforming serves three purposes: the increased temperature resulting from the partial combustion and subsequent adiabatic reforming results in a greater amount of reforming so that the secondary reformed gas contains a decreased proportion of residual methane. Secondly the increased temperature favours the reverse shift reaction so that the carbon monoxide to carbon dioxide ratio is increased. Thirdly the partial combustion effectively
20 consumes some of the hydrogen present in the reformed gas, thus decreasing the hydrogen to carbon oxides ratio. In combination, these factors render the secondary reformed gas formed from natural gas as a feedstock more suited for use as synthesis gas for applications such as Fischer-Tropsch synthesis than if the secondary reforming step was omitted. Also more high grade heat can be recovered from the secondary reformed gas: in particular, the recovered heat can be used to heat the catalyst-containing tubes of the primary reformer. Thus the
25 primary reforming may be effected in a heat exchange reformer in which the catalyst-containing reformer tubes are heated by the secondary reformed gas. Examples of such reformers and processes utilising the same are disclosed in for example US 4 690 690 and US 4 695 442.

It has been proposed in WO 00/09441 to employ a reforming process wherein the feedstock/steam mixture is subjected to primary reforming over a catalyst disposed in heated
30 tubes in a heat exchange reformer, the resultant primary reformed gas is then subjected to secondary reforming by partially combusting the primary reformed gas with an oxygen-containing gas and bringing the resultant partially combusted gas towards equilibrium over a secondary reforming catalyst, and then the resultant secondary reformed gas is used to heat the tubes of the heat exchange reformer. In the aforesaid WO 00/09441 carbon dioxide was
35 separated from the product, before or after use thereof for the synthesis of carbon containing compounds, and recycled to the reformer feed. In one embodiment described in that reference, the recycled carbon dioxide was part of the tail gas from a Fischer-Tropsch

synthesis process, and was added to the natural gas feedstock prior to desulphurisation of the latter.

The Fischer-Tropsch tail gas is liable to contain a significant amount of carbon monoxide. If this is added to the feedstock prior to primary reforming in a heat exchange reformer, the carbon monoxide undergoes the exothermic methanation reaction resulting in a faster increase in temperature of the gas undergoing reforming than if the tail gas had not been added. The temperature difference between the gas undergoing reforming and the heating medium is thus decreased and so more heat transfer area, e.g. more and/or longer heat exchange tubes, is required for a given reforming duty.

We have realised that by addition of the tail gas to the primary reformed gas before partial combustion thereof, this problem may be overcome.

Accordingly the present invention provides a process for the production of hydrocarbons by the Fischer-Tropsch reaction comprising

- a) subjecting a mixture of a hydrocarbon feedstock and steam to steam reforming by
 - i) passing the mixture over a catalyst disposed in heated tubes in a heat exchange reformer to form a primary reformed gas,
 - ii) subjecting the primary reformed gas to secondary reforming by partially combusting the primary reformed gas with an oxygen-containing gas and bringing the resultant partially combusted gas towards equilibrium over a secondary reforming catalyst, and
 - iii) using the resultant secondary reformed gas to heat the tubes of the heat exchange reformer, thereby producing a partially cooled reformed gas,
 - b) further cooling the partially cooled reformed gas to below the dew point of the steam therein to condense water and separating condensed water to give a de-watered synthesis gas,
 - c) synthesising hydrocarbons from said de-watered synthesis gas, and separating at least some of the synthesised hydrocarbons, to give a tail gas, and
 - d) recycling at least part of said tail gas to the step a)
- characterised in that the recycled tail gas is added to the primary reformed gas before partial combustion thereof.

The amount of oxygen required in the secondary reformer is determined by two main considerations, viz. the desired composition of the product gas, and the heat balance of the heat exchange reformer. In general, increasing the amount of oxygen causes the $[H_2] / [CO]$ ratio to decrease and the proportion of carbon dioxide to decrease. Alternatively, if the conditions are arranged such that the product composition and temperature is kept constant, increasing the temperature at which the feedstock is fed to the heat exchange reformer decreases the amount of oxygen required (at a constant oxygen feed temperature). Decreasing the required amount of oxygen is advantageous as this means that a smaller, and

hence cheaper, air separation plant can be employed to produce the oxygen. The temperature of the feedstock can be increased by any suitable heat source, which may, if necessary, be a fired heater, which of course can use air, rather than oxygen, for the combustion.

In an alternative embodiment of the invention, carbon dioxide is separated from the synthesis gas prior to the Fischer-Tropsch synthesis stage and recycled to the synthesis gas production. This recycled carbon dioxide stream may be added, as in the aforesaid WO 00/09441, to the feedstock prior to feeding the latter to the heat exchange reformer or to the primary reformed gas before the latter is fed to the secondary reforming step. In either case, some or all of the Fischer-Tropsch tail gas, which will contain hydrogen, carbon monoxide and lower hydrocarbons such as methane and ethane, is added to the primary reformed gas before feeding the latter to the secondary reforming step.

Where the recycled carbon dioxide (either as carbon dioxide separated from the synthesis gas prior to synthesis and recycled, or as the recycled tail gas) is added to the primary reformed gas, rather than to the feedstock prior to primary reforming, there is an advantage that the primary reforming process can be operated at a lower steam ratio. [By the term "steam ratio" we mean the ratio of the number of moles of steam to the number of gram atoms of hydrocarbon carbon in the feed: thus a methane/steam mixture comprising 2 moles of steam per mole of methane has a steam ratio of 2.] Thus in the primary reforming stage, there is a risk that carbon will be deposited on the primary reforming catalyst. At any given temperature, the risk of carbon deposition is decreased by decreasing the proportion of carbon dioxide in the feed and also by increasing the steam ratio. Hence if the recycled carbon dioxide is not added until after the primary reforming, the risk of carbon deposition is decreased and so the process can be operated at a lower steam ratio. For example if the feedstock is methane and amount of recycled carbon dioxide is 0.2 moles per mole of methane feed, at a primary reforming exit temperature of 750°C, adding the recycled carbon dioxide after primary reforming, rather than before primary reforming, enables the steam ratio to be reduced by about 0.2, e.g. from about 0.9 to about 0.7, before there is a serious risk of carbon deposition.

The invention is illustrated by reference to the accompanying drawing which is a diagrammatic flowsheet of one embodiment of the invention.

In the drawing, a mixture of a desulphurised hydrocarbon feedstock, for example natural gas, and steam is fed, typically at a pressure in the range 10 to 50 bar abs., via line 10 to a heat exchanger 12 and thence, via line 14, to the catalyst-containing tubes 16 of a heat exchange reformer 18. The mixture is typically heated to a temperature in the range 350 to 550°C prior to entry into the tubes 16. For simplicity only one tube is shown in the drawing: in practice there may be several tens or hundreds of such tubes.

The feedstock/steam mixture undergoes primary steam reforming in the tubes 16 and the primary reformed gas leaves the heat exchange reformer 18 via line 20, typically at a temperature in the range 600 to 800°C. The primary reformed gas is mixed with Fischer-

Tropsch tail gas (to be described) fed via line 22 and the mixture is fed via line 24 to a secondary reformer 26, to which oxygen is supplied via line 28.

The primary reformed gas/tail gas mixture is partially combusted in the secondary reformer and brought towards equilibrium by passage over a secondary reforming catalyst.

5 The secondary reformed gas leaves secondary reformer via line 30, typically at a temperature in the range 850 to 1150°C.

Heat is recovered from the hot secondary reformed gas by passing the secondary reformed gas via line 30 to the shell side of the heat exchange reformer 18 so that the secondary reformed gas forms the heating medium of the heat exchange reformer. The secondary reformed gas is thus cooled by heat exchange with the gas undergoing reforming in the tubes 16 and leaves the heat exchange reformer via line 32, typically at a temperature 50 to 150°C above the temperature at which the hydrocarbon feedstock/steam mixture is fed to the tubes 16.

The partially cooled secondary reformed gas is then cooled further with heat recovery in one or more heat exchangers 34 to a temperature below the dew point of the water in the secondary reformed gas. The cooled secondary reformed gas is then fed via line 36 to a separator 38 wherein condensed water is separated as a liquid water stream 40. This water can be recycled by heating it and contacting the hydrocarbon feedstock with the resultant hot water in a saturator to provide the feedstock/steam mixture.

20 The remaining de-watered gas is then fed, via line 42, to an optional hydrogen separation unit 44, e.g. a membrane unit or a pressure swing adsorption stage, to separate part of the hydrogen in the de-watered gas as a hydrogen stream 46. The resultant gas is then fed via line 48 to a Fischer-Tropsch synthesis stage 50, wherein liquid hydrocarbons are synthesised and are separated, together with by-product water, as a product stream 52 leaving a tail gas stream 54. Part of the tail gas is purged as stream 56 to avoid a build up of inerts, e.g. nitrogen which may be present in the hydrocarbon feedstock as a contaminant and/or is often present in small amounts as an impurity in the oxygen used for the partial combustion. The purged tail gas may be used as fuel, for example in a fired heater heating the mixture of hydrocarbon and steam fed to the heat exchange reformer. The remainder of the tail gas is fed to a compressor 58 and then to a heat exchanger 60 and then fed via line 22 to be mixed with the primary reformed gas.

35 The invention is further illustrated by the following calculated example of a process in accordance with the above flowsheet. In the following table the pressures (P, in bar abs.), temperatures (T, in °C) and flow rates (kmol/h) of the various components of the streams are quoted, rounded to the nearest integer.

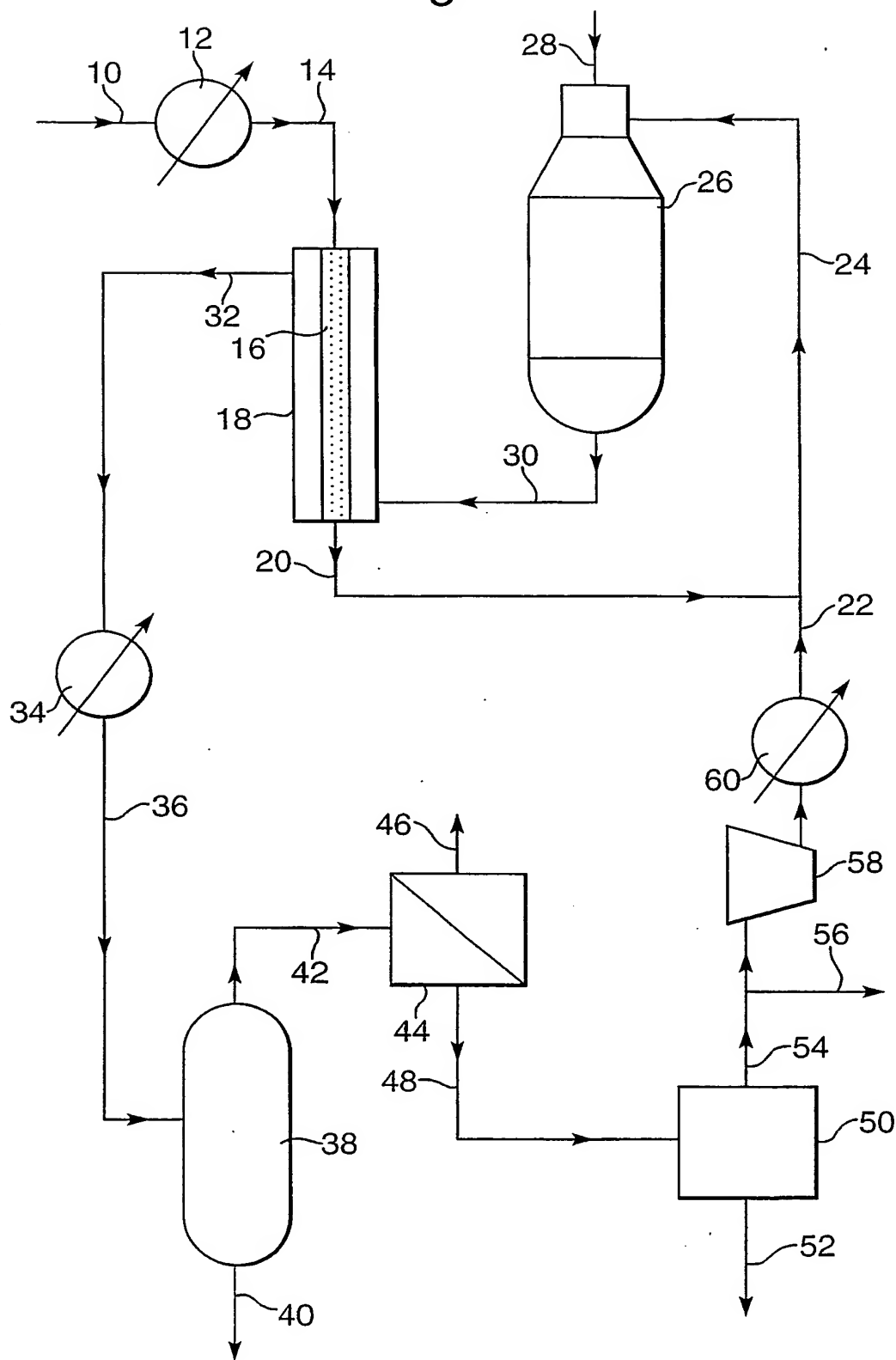
Stream	P (bara)	T (°C)	Flow rate (kmol/h)						
			CH ₄	CO	CO ₂	H ₂	H ₂ O	O ₂	N ₂
14	34	425	4421 ^a	0	101	0	6605	0	20
20	31	750	4808	1157	977	5498	3687	0	20
22	31	170	247 ^b	718	1044	1159	0	0	50
24	31	663	5055 ^b	1885	2021	6657	3687	0	70
28	31	20	0	0	0	0	0	3269	16
30	30	1050	215	7451	1501	14601	5698	0	86
32	30	520	215	7451	1501	14601	5698	0	86
46	1	50	0	0	0	360	0	0	0
48	26	50	215	7451	1501	14241	97	0	86
52	24	50	0 ^e	0	0	0	5737	0	0
54	24	50	423 ^c	1231	1791	1988	0	0	86
56	24	50	176 ^d	513	747	829	0	0	36
^a also contains 2430 kmol/h of higher hydrocarbons expressed as CH _{2.76} ^{b, c, d} also contain 204, 354 and 150 kmol/h respectively of higher hydrocarbons expressed as CH _{2.67} ^e also contains 5368 kmol/h of higher hydrocarbons expressed as CH _{2.13}									

- By way of comparison, if the tail gas stream 22 was added to the primary reformer feed 14 instead of to the primary reformed gas leaving the heat exchange reformer, in order to obtain the same amount of synthesis gas, the amount of oxygen required is 3360 kmol/h, i.e.
- 5 an increase of 2.8%, or, if the amount of oxygen is not increased, the heat transfer area in the heat exchange reformer has to be increased in size by 25%.

Claims

1. A process for the production of hydrocarbons by the Fischer-Tropsch reaction comprising
 - a) subjecting a mixture of a hydrocarbon feedstock and steam to steam reforming by
 - i) passing the mixture over a catalyst disposed in heated tubes in a heat exchange reformer to form a primary reformed gas,
 - ii) subjecting the primary reformed gas to secondary reforming by partially combusting the primary reformed gas with an oxygen-containing gas and bringing the resultant partially combusted gas towards equilibrium over a secondary reforming catalyst, and
 - iii) using the resultant secondary reformed gas to heat the tubes of the heat exchange reformer, thereby producing a partially cooled reformed gas,
 - b) further cooling the partially cooled reformed gas to below the dew point of the steam therein to condense water and separating condensed water to give a de-watered synthesis gas,
 - c) synthesising hydrocarbons from said de-watered synthesis gas, and separating at least some of the synthesised hydrocarbons, to give a tail gas, and
 - d) recycling at least part of said tail gas to the step a),characterised in that the recycled tail gas is added to the primary reformed gas before partial combustion thereof.
2. A process according to claim 1 wherein carbon dioxide is separated from the synthesis gas prior to synthesis of the hydrocarbons and is added to the hydrocarbon feedstock/steam mixture prior to steam reforming.
3. A process according to claim 1 wherein carbon dioxide is separated from the synthesis gas prior to synthesis of the hydrocarbons and is added to the primary reformed gas before combustion thereof.

Fig.1.



SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

Internat'l Application No

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C27/06 C01B3/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01 42175 A (RYTTER ERLING ; SCHANKE DAG (NO); SOGGE JOSTEIN (NO); HANSEN ROGER) 14 June 2001 (2001-06-14) page 8, line 23 -page 10, line 21; claims 1,5	1-3
A	WO 00 09441 A (ABBOTT PETER EDWARD JAMES ; ICI PLC (GB)) 24 February 2000 (2000-02-24) cited in the application claims 1-4	1-3
A	DE 739 569 C (BRAUNKOEHLE BENZIN AG) 4 October 1943 (1943-10-04) page 1, line 10 -page 2, line 21 -/-	1-3

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 168 719 A (HUMPHREYS & GLASGOW LTD) 25 June 1986 (1986-06-25) page 1, line 13 - line 42; claims 1,2 -----	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Publication No

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